PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : D21C 5/00, 9/08

A1

(11) International Publication Number: WO 92/16687

(43) International Publication Date: 1 October 1992 (01.10.92)

(21) International Application Number: PCT/FI92/00076

(22) International Filing Date: 19 March 1992 (19.03.92)

(30) Priority data:
911410 22 March 1991 (22.03.91) FI

(71) Applicant *(for all designated States except US):* GENENCOR INTERNATIONAL EUROPE OY [FI/FI]; Kyllikinportti 2, P.O. Box 105, SF-00241 Helsinki (FI).

(72) Inventors; and
(75) Inventors/Applicants *(for US only) :* JOKINEN, Olli [FI/FI]; Rajakalliontie 17 B, SF-02460 Kantvik (FI). HAGSTRÖM-NÄSI, Christine [FI/FI]; Klaarantie 9 A 9, SF-00200 Helsinki (FI).

(74) Agent: OY KOLSTER AB; Stora Robertsgatan 23, P.O. Box 148, SF-00121 Helsinki (FI).

(81) Designated States: AT (European patent), AU, BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), MC (European patent), NL (European patent), SE (European patent), US.

Published
With international search report.

(54) Title: A METHOD FOR REDUCING PITCH TROUBLE IN MECHANICAL PULP

(57) Abstract

The invention relates to a method for reducing the pitch trouble of mechanical pulp and/or papermaking pulp containing mechanical pulp by treating the pulp or white water with a cellulase/hemicellulase enzyme preparation.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria
AU	Australia
BB	Barbados
BE	Belgium
BF	Burkina Faso
BG	Bulgaria
BJ	Benin
BR	Brazil
CA	Canada
CF	Central African Republic
CG	Congo
CH	Switzerland
CI	Côte d'Ivoire
CM	Cameroon
CS	Czechoslovakia
DE	Germany
DK	Denmark
ES	Spain
FI	Finland
FR	France
GA	Gabon
GB	United Kingdom
GN	Guinea
GR	Greece
HU	Hungary
IE	Ireland
IT	Italy
JP	Japan
KP	Democratic People's Republic of Korea
KR	Republic of Korea
LI	Liechtenstein
LK	Sri Lanka
LU	Luxembourg
MC	Monaco
MG	Madagascar
ML	Mali
MN	Mongolia
MR	Mauritania
MW	Malawi
NL	Netherlands
NO	Norway
PL	Poland
RO	Romania
RU	Russian Federation
SD	Sudan
SE	Sweden
SN	Senegal
SU	Soviet Union
TD	Chad
TG	Togo
US	United States of America

A method for reducing pitch trouble in mechanical pulp

The invention relates to a method for reducing pitch trouble in mechanical pulp and/or papermaking pulp containing mechanical pulp by a cellulase/hemicellulase treatment.

Mechanical pulps include groundwood pulp, refiner mechanical pulp, pressure groundwood, thermomechanical pulp and chemi-thermomechanical pulp (CTMP). In the production of mechanical pulp, fibres are detached from the wood mainly mechanically by utilizing heat. The fibre is subjected to stress so that the lignin binding fibres together is softened, and the fibres are detached from each other when the elasticity of lignin fails.

Wood contains about 1 to 10% of pitch and extractants soluble in organic solvents in addition to its main components (cellulose, hemicellulose and lignin). Pitch contains fatty acids, resin acids, glycerides, etc. It is well-known that the pitch content in softwood, which is the primary raw material of mechanical pulp, is high as compared with hardwood, for instance. At the pulp production stage, pitch components are separated from the pulp into a free space, e.g., in the white water. Pitch suspended in the white water is in the form of particles 0.2 to 2 µm in diameter, also known as colloidal pitch.

In papermaking, pitch may deposit on pipes, containers, wires or presses, causing such pitch troubles as inferior paper quality (e.g. holes and spots) and paper breakages. It may also block felts and wires, hampering the removal of water from a paper web. Pitch troubles may also lead to long production stoppages. They occur frequently

especially when stock containing plenty of mechanical pulp is used as raw material.

Traditionally, wood has been stored outdoors for long periods of time (3 to 6 months or more) in an attempt to avoid pitch trouble. In this way, pitch components are degraded mainly by the oxidizing effect of air. Such inorganic substances as talc and anionic surfactants that disperse pitch particles have also been used in the prevention of pitch trouble.

FI Patent Application 870072 discloses a pitch prevention method which utilizes certain water-soluble polyquaternary amines. These compounds are added to the pulp or paper making system to avoid pitch trouble.

FI Patent Application 900679 discloses a method for reducing the pitch content of wood by means of fungi degrading the pitch and resin components present in wood.

FI Patent Application 895901 discloses a method for avoiding pitch trouble associated with mechanical pulp by adding acylglycerol lipase enzyme to the stock or white water. This enzyme degrades triglycerides contained in pitch.

The use of enzymes, including cellulase and hemicellulase, for improving the properties of pulp is known *per se*. For example, FR Patent Specification 2557894 discloses a method for treating cellulose pulp by xylanase in order to shorten the beating time. CA Patent Specification 758488 concerns a method for improving the beatability of pulp by a cellulase/pectinase/lipase treatment. FR Patent Specification 2571738 concerns a method in which pulp is provided with special pulp properties by cellulase treatment.

FI Patent Application 874113 (corresponds to FR Patent Application 8613208) relates to a method for improving the properties of recycled pulp, for instance, (in this particular case a pulp containing plenty of chemical pulp) by cellulase/hemicellulase treatment. FI Published Specification 81394, in turn, aims at improving the drainability of mechanical pulp by hemicellulase treatment (no cellulase).

In addition, FI Patent Application 890214 describes treatment of the white water of a paper-making system by enzymes for degrading components dissolved or dispersed from the pulp, such as hemicellulose.

The object of the invention is to develop a method for reducing pitch trouble associated with the production of mechanical pulp, especially papermaking pulp containing mechanical pulp. Methods known from the prior art have been used with varying success, and problems have not been completely avoided.

It has now been unexpectedly discovered that the pitch trouble associated with the production of mechanical pulp can be reduced substantially by a cellulase/hemicellulase treatment. In the pulp filtrate water, there occurred an abrupt decrease in the extractant concentrations indicating the pitch content, especially in the fatty acid, resin acid and sterol concentrations, and the turbidity of the filtrate water was reduced.

In accordance with the invention, the pitch trouble associated with the production of mechanical pulp and/or papermaking pulp containing mechanical pulp is solved by treating the mechanical pulp, papermaking pulp containing mechanical pulp and/or white water by an enzyme preparation containing cellulase/hemicellulase enzyme activity.

It was fully unexpected that the cellulase and hemicellulase enzymes, which, as is well-known, degrade cellulose and hemicellulose, also affect the main components of pitch, that is, fatty acid, resin acid and sterol type substances.

In practice, the reduction in the pitch trouble become apparent e.g. in that the runability of the paper machine was improved, the wires and felts remained clean, and the number of holes and spots in paper was decreased.

The enzyme treatment had also other advantageous effects. For example, the drainability of pulp was improved. The enzyme treatment did not either deteriorate the optical or printing properties of the pulp but its brightness, light scattering coefficient, compressibility and smoothness were improved.

The enzyme treatment according to the invention can be performed at any pulp production stage after the mechanical detachment of fibres. The enzyme can be added e.g. to a pulp storing container, storage tower or metering chest. The enzyme treatment can be performed before the bleaching of pulp, in connection with a pulp bleaching process or after the bleaching. The enzyme can also be added to the white water.

The cellulase/hemicellulase enzymes for the use in accordance with the invention can be produced in a known manner by means of actinomycetes, bacteria and fungi.

It is also possible to use commercial cellulase/hemicellulase preparations, such as Liftase A40 (manufacturer Genencor International Europe Ltd.), produced by the fungus *Trichoderma longibrachiatum* and having a CMCase activity (carboxymethyl cellulase activity) of 2,500 U/ml, a filter

paper activity (FPU activity) of 110 U/ml and a xylanase activity of 500 U/ml. The carboxymethyl cellulase activity and the filter paper activity describe the cellulolytic activity, and the xylanase activity describes the hemicellulolytic activity.

The determination of the filter paper activity is described in Ghose, T.K., Patnak, A.N., Bisaria, V.S., Symposium of Enzymatic Hydrolysis of Cellulose, Bailey, M., Enari, T.M., Linko, M., Eds. (SITRA, Aulanko, Finland, 1975), 111 - 136; the determination of the CMCase activity is described in Mandels, M., Weber, J., Adv. Chem. Ser. 95 (1969) 391-413; and the determination of the xylanase activity is described in Khan, A.W., Tremblay, D., LeDuy, A., Enzyme Microb. Technol., 8 (1986) 373 - 377.

Other cellulase/hemicellulase preparations of the same manufacturer (Genencor International Europe Ltd), such as Multifect L250 and Cytolase 123, and cellulase/hemicellulase preparations from other manufacturers can also be used.

Suitable enzyme dosages given as enzyme activities per kg of pulp dry solids are within the following limits (U = activity unit):

Cellulases:	
Filter paper activity	1 - 20,000 U/kg pulp
CMCase activity	10 - 500,000 U/kg pulp
Hemicellulases:	
Xylanase	0 - 2,000,000 U/kg pulp

Preferred enzyme dosages are:

Filter paper activity	about 20 - 600 U/kg pulp
CMCase activity	about 500 - 10,000 U/kg pulp
Xylanase activity	about 500 - 100,000 U/kg pulp.

The enzyme treatment is usually carried out

within the pH range from about 2 to 10, preferably within the range from about 4 to 8. The temperature of the enzyme treatment may range from about 10 to 90°C, preferably from about 25 to 70°C.

In the following the invention will be described more closely by means of working examples based on laboratory experiments and mill test runs. The examples are merely illustrative and they are not intended to restrict the invention. The measurements were performed in compliance with the SCAN standards, if not stated otherwise.

Example 1

Thermomechanical pulp (TMP) produced from spruce (Picea abies) and having a consistency of 4%, pH 4.9, a freeness value of 69 ml CSF and ISO brightness of 66% was taken from a mill process and treated with an enzyme preparation called Liftase A40. Liftase A40 (manufacturer Genencor International Europe Ltd.) is produced by means of the *Trichoderma longibrachiatum* microorganism and the principal activities contained in it are as follows:

CMCase activity	2,500 U/ml
FPU activity	110 U/ml
Xylanase activity	500 U/ml

Liftase A40 enzyme was added under careful mixing to the pulp at 55°C in an amount corresponding to 2.5 l/ton of pulp dry solids.

The dosages of the added enzyme preparation given as cellulase/hemicellulase activities per kg pulp dry solids were as follows:

CMCase activity	6,250 U/kg
FPU activity	275 U/kg
Xylanase activity	1,250 U/kg

The enzyme was allowed to react with the pulp at 55°C and pH 4.9 while mixing the pulp at 150 rpm for one hour altogether. Samples were taken from the pulp at uniform intervals, and the samples were determined for turbidity and the final sample also for extractant concentrations. In the liquid fraction of TMP, turbidity is caused by extractants (pitch), suspended carbohydrates and other small components detached from the pulp. Accordingly, the turbidity describes approximately changes associated with all the above-mentioned components. Separate analysis of the extractants gives a more accurate result specifically as far as pitch is concerned. For turbidity measurement, 250 g of the pulp suspension was centrifuged (1,800 rpm, 20 min). The supernatant (liquid fraction) was recovered and measured immediately for the turbidity with a Novasine Analite NTM-150 turbidity meter. Extractants present in the supernatant were measured by gas chromatography.

A control sample was treated in a similar way as the enzyme-treated sample but without enzyme.

The measuring results are shown in Table 1.

Table 1

Effect of enzyme treatment on the turbidity and extractant concentrations of the liquid fraction of TMP

	CONTROL	ENZYME TREATED
TURBIDITY, NTU		
- 0 min	320	320
- 10 min	300	190
- 30 min	310	100
- 60 min	330	25

EXTRACTANTS, mg/l		
60 min		
- fatty acids	65	6.2
- resin acids	21	2.5
- sterols	13	1.2

The results show that a significant reduction in the turbidity of the liquid fraction of the pulp occurs as soon as after a reaction time of 10 minutes. After a reaction time of 60 min, the liquid fraction is almost clear, that is, has a turbidity of 25 NTU, and the concentration of extractants in the liquid fraction has decreased to 1/10 of the original value. This indicates that the extractants are deposited on or adhere to the surface of the fibre due to the enzyme treatment.

Example 2.

The practical significance of the reduction in the pitch content of the filtrate water of mechanical pulp was to be determined, that is, a mill test run was carried out. The test run was carried out on an LWC machine applying on-machine coating.

The mechanical pulp used in the machine was peroxide bleached TMP, and as the experiments in Example 1 were performed on unbleached TMP, a laboratory check experiment series was performed before the test run. Peroxide bleached TMP was derived directly from a process with a consistency of 3.2%. The pH of the pulp was 5.5 and temperature 45°C. Under these conditions, the pulp was subjected to an enzyme treatment by using the Liftase A40 enzyme in an amount of 2 l/t. The pitch content was estimated by a turbidity measurement. For measurement, the pulp was filtered through a Macherey-Nagel

MN 640 w filter paper, and turbidity was measured with the meter mentioned in Example 1. The results with different reaction times are shown in the table below.

Reaction time (min)	Turbidity (NTU)
0	323
40	110
120	28

As is to be seen, the enzyme was extremely effective, and the mill test run could be started.

The duration of the test run was 6 days and the enzyme was Liftase A40 with a dosage of 2 l/t TMP. The enzyme was dosed to the suction side of a pump pumping peroxide bleached TMP from a storage tower into a so-called refiner mechanical pulp chest. The enzyme treatment conditions in the chest were as follows:

- pH 5.5
- temperature, °C 45
- consistency, % 3.5
- reaction time, min 42

After the refiner mechanical pulp chest the peroxide bleached TMP was mixed with chemical pulp and reject in a mixing chest. Then the pulp mixture was pumped into a machine chest and further after wire water dilution into the head box of a paper machine. During the test run the pitch content was estimated by measuring the turbidity of the filtrate water of TMP, in addition to which the freeness of TMP was measured. The results are shown in the table below.

	CONTROL	ENZYME
Filtrate turbidity, NTU		
- before refiner pulp chest	370	370
- after refiner pulp chest	420	250
Freeness, ml		
- before refiner pulp chest	62	62
- after refiner pulp chest	59	65

It appears from the results that the enzyme is effective also in mill conditions and the obtained reduction in turbidity is 170 units, which indicates a marked decrease in the pitch content in the filtrate, i.e. that the pitch has adhered to or deposited on the fibres. It is also to be seen that the freeness of TMP has increased by 6 units, which means that the removal of water is easier.

During the test run the following observations suggesting that the pitch trouble was eliminated/reduced were made on the machine:

- The runability of the machine was exceptionally good throughout the enzyme period.
- The wires and felts and the entire wire section remained very clean.
- The number of holes and spots in base paper decreased clearly as compared with a normal run.

The results of the test run were verified by a repeat test run having a duration of 10 days. As to the pitch and runability, the results complied with those of the first test run. In addition, it was observed that the enzyme treatment has a positive effect on the function of the conventional retention agent, as the target level of retention was achieved with a dosage of retention agent which was 20 to 30%

smaller than normally.

Example 3

The increase in the freeness of mechanical pulp observed in the mill test run raised a question about its effect on the optical and printing properties of the pulp primarily in view of the use of the enzyme-treated pulp in uncoated paper qualities, such as SC paper and newsprint. To study this, a sample was obtained from a typical mechanical pulp i.e. groundwood for SC paper. The pulp was subjected to an enzyme treatment under conditions given in Table 2 with different dosages of Liftase A40. After the enzyme treatment, laboratory sheets were prepared from the pulp. Properties measured from the sheets both immediately and after calendering are also shown in Table 2. As can be seen from the results, the enzyme treatment did not deteriorate the optical or printing properties of the pulp even though the increase in the freeness value was as high as 25 units; in fact, the effect was the opposite as

- the light absorption coefficient decreased, which indicates improved brightness,
- the light scattering coefficient improved,
- the compressibility increased (density after calendering), and
- the smoothness improved (roughness decreased).

Accordingly, enzyme-treated pulp can well be used in uncoated paper qualities. The enzyme treatment not only reduces the pitch trouble but it can also be expected to improve the quality of the paper either directly or at least in that the fineness of the mechanical pulp can be increased and inferior water removal can be compensated for by enzyme treatment.

Example 4.

To verify the obtained results, tests were carried out both on unbleached TMP and dithionite bleached TMP, and not only the effect on the pitch content (turbidity) but also the effects on the water removal (freeness), water retention ability (WRV) and sheet properties were measured. This time the sheets were prepared by using a so-called white water sheet mould. The enzyme treatment conditions and the obtained results appear from Table 3. As is to be seen, the effect of the enzyme treatment on pitch content (turbidity) also became apparent with these pulps. In addition, the following positive effects were observed:

- water removal properties are improved (freeness increases and WRV decreases);
- optical properties are improved (light scattering coefficient and brightness increase),
- printing properties are improved (roughness decreases and compressibility increases, that is, density after calendering increases).

Example 5.

As it was observed that the enzyme treatment has a positive effect on the brightness of mechanical pulp, it was decided to study the effect of enzyme treatment carried out before bleaching. For this purpose, the pulps described in Example 1 (control and enzyme-treated) were peroxide bleached with different amounts of peroxide under normal peroxide bleaching conditions (consistency 16%, temperature 60°C, reaction time 90 min, DTPA 0.2%, $MgSO_4 \cdot 7H_2O$ 0.5% and Na-silicate 5% on pulp). After bleaching the pulps were measured for brightness immediately and after ageing. The results are shown in Figure 1. It can be seen that the brightness has improved and the improvement

is to be seen also after ageing. As a consequence, it can be stated that the enzyme treatment has a positive effect also on the bleachability of mechanical pulp.

Example 6.

The positive effect of the enzyme on the function of the conventional retention agent observed in the mill test run was verified by a laboratory experiment. Unbleached TMP from an intermediate container of mechanical pulp was treated with Liftase A40 under the following conditions:

- pH 5.0
- temperature 50°C
- reaction time 1 hour
- pulp consistency 3.7%
- enzyme dosage 0, 1, 2 and 4 l/t TMP.

Corresponding enzyme dosages given as cellulase/hemicellulase activities per kg pulp dry solids were as follows:

	1 l/t (U/kg)	2 l/t (U/kg)	4 l/t (U/kg)
CMCase activity	2,500	5,000	10,000
FPR activity	110	220	440
Xylanase activity	500	1,000	2,000

After the enzyme treatment, TMP was mixed with chemical pulp and kaolin under the following conditions:

- TMP 42%
- chemical pulp 24%
- kaolin 33%.

The pulp mixture was diluted to a concentration of about 10 g/l. The dry solids content and fine solids content of the mixture were determined as well

as its total, fine solids and ash retention with a Dynamic Drainage Jar device in accordance with the TAPPI T261 pm-80 method. The retention measurement was carried out on the mixture as such and after an addition of the retention agent.

The obtained results appear from Table 4. It is seen that the enzyme treatment does improve the retention, that is, in practice, the function of the conventional retention agent is made more effective, and when aiming at constant retention, the amount of the conventional retention agent can be decreased.

Table 2.

Pulp: 100% SC groundwood, 52 CSF
Enzyme treatment conditions:
Temperature: 40°C
pH 5.0
Reaction time: 1 h
Consistency: 2%

	Liftase A40, l/t			
	0	1	2	4
Freeness after enzyme treatment	52	59	66	77
Laboratory sheets/before calendering				
- grammage, g/m^2	107	107	106	106
- density, kg/m^3	375	372	369	371
- tear index, mNm^2/g	3.78	3.91	3.93	3.85
- tensile index, Nm/g	29.8	28.3	28.1	26.9
- elongation, %	2.9	2.9	3.1	3.0
- burst index, $kPam^2/g$	1.57	1.42	1.41	1.31
- G-H porosity, S/100 ml	51	47	44	38
- light scattering coefficient, m^2/kg	74.4	74.7	74.7	74.6
- light absorption coefficient, m^2/kg	3.38	3.02	2.93	2.86
Laboratory sheets/after calendering (2 x 200 kN/m)				
- grammage, g/m^2	106	107	105	105
- density, kg/m^3	630	648	661	665
- roughness, PPS_{10}, µm	2.82	2.74	2.60	2.56
- Bendtsen air permeability ml/min	70	68	80	86
- Cobb-Unger oil absorption, g/m^2	19.2	20.4	19.7	20.5

Table 3.

Enzyme treatment of unbleached and dithionite bleached TMP

Treatment conditions: pH 4.9 (unbleached TMP); and 5.0 (dithionite bleached TMP), temperature 55°C, reaction time 1 h, consistency 3%.

	Unbleached TMP			Dithionite bleached TMP		
Enzyme dosage, l/t	0	0.75	2.0	0	0.75	2.0
Turbidity, NTU	205	180	80	210	160	70
CSF, ml	56	60.5	65.5	54.5	58.5	67.5
WRV, %	116	112	109	118	116	110
Grammage, g/m^3	65.1	65.3	65.2	65.1	65.4	65.6
Density, kg/m^3	397	400	411	399	413	399
Tear index, mNm^3/g	7.18	7.20	7.12	6.92	6.94	6.92
Burst index, $kPam^3/g$	2.75	2.28	2.19	2.69	2.41	2.19
Tensile index, Nm/g	39.1	33.9	34.7	40.8	36.5	33.9
Elongation, %	2.8	2.4	2.7	3.0	2.3	2.3
Porosity, Gurley-Hill, s/100 ml	98	89	89	103	121	96
Brightness, % ISO	62.6	64.1	64.2	67.6	67.2	67.7
Light scattering coefficient, m^2/kg	62.9	63.1	63.5	64.0	64.8	66.5
Light absorption coefficient, m^2/kg	2.59	2.16	2.13	1.62	1.70	1.64

After calendering (2 x 200 kN/m):

	Unbleached TMP			Dithionite bleached TMP		
Grammage, g/m^2	65.5	65.0	65.5	65.3	65.5	65.7
Density, kg/m^2	675	683	675	672	686	680
Roughness, PPS_{10}, m						
- top	2.64	2.29	2.32	2.43	2.42	2.22
- wire	2.68	2.50	2.52	2.73	2.66	2.59
Air permeability, Bendsten, ml/min	110	120	120	110	120	120
Oil absorption, Unger, g/m^2	10.3	10.5	10.8	10.5	9.9	10.9

Table 4.

Effect of enzyme treatment on retention.

Enzyme treatment conditions: pH 5.0, temperature 50°C, reaction time 1 h, consistency 3.7%, enzyme dosage 0-4 l/t TMP.

Liftase A40 l/t TMP	Retention agent*	Retention %		
		Total retention	Fine solids retention	Filler retention
-	-	61.8	43.5	6.0
-	+	64.6	47.6	15.9
1	-	66.3	50.2	14.7
1	+	67.0	51.3	20.1
2	-	63.9	44.8	10.7
2	+	67.2	48.0	19.5
4	-	64.0	45.4	8.8
4	+	66.9	50.0	17.7

* Fennopol K 211 155 g/t dry solids

Claims:

1. A method for reducing the pitch trouble in mechanical pulp and/or papermaking pulp containing mechanical pulp, characterized in that the mechanical pulp, papermaking pulp containing mechanical pulp and/or white water is/are treated with an enzyme preparation containing cellulase/hemicellulase enzyme activity.

2. A method according to claim 1, characterized in that the pulp is groundwood, refiner mechanical pulp, pressure groundwood, thermomechanical pulp or chemi-thermomechanical pulp.

3. A method according to claim 1 or 2, characterized in that the pulp is unbleached pulp.

4. A method according to claim 1 or 2, characterized in that the pulp is bleached pulp.

5. A method according to claim 4, characterized in that the enzyme treatment is carried out before the bleaching of pulp.

6. A method according to claim 4, characterized in that the enzyme treatment is carried out after the bleaching of pulp.

7. A method according to any of the preceding claims, characterized in that the enzyme preparation is added in an amount corresponding to 1 - 20,000 units of cellulolytic activity determined as filter paper activity, 10 - 500,000 units of cellulolytic activity determined as CMCase activity, and 0 - 2,000,000 units of hemicellulolytic activity determined as xylanase activity per kg pulp dry solids.

8. A method according to claim 7, characterized

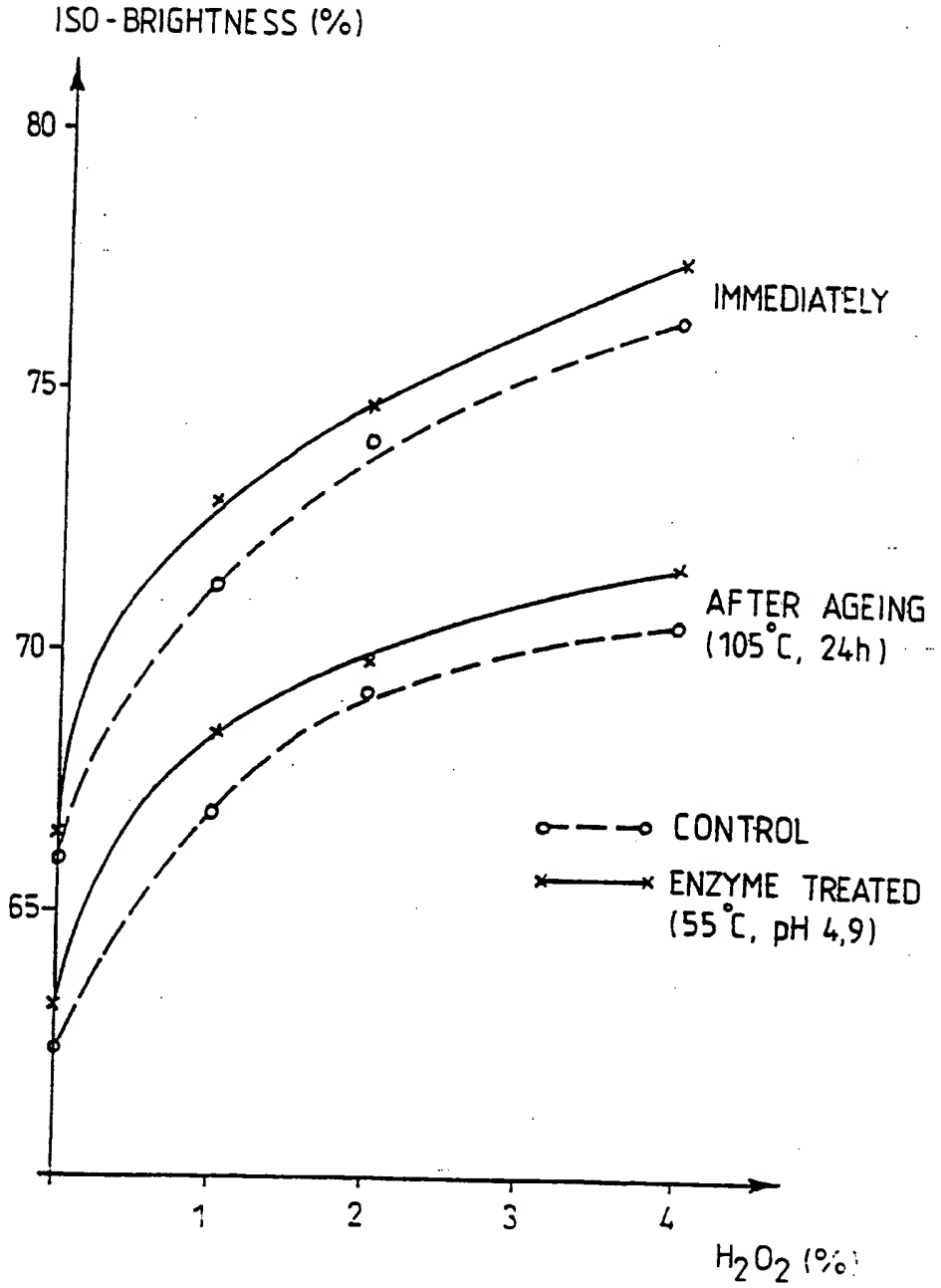
terized in that the enzyme preparation is added in an amount corresponding to about 20 - 600 units of cellulolytic activity determined as filter paper activity, about 500 - 10,000 units of cellulolytic activity determined as CMCase activity, and about 500 - 100,000 units of hemicellulolytic activity determined as xylanase activity.

9. A method according to any of the preceding claims, characterized in that the enzyme treatment is carried out within the pH range of about 2-10.

10. A method according to claim 9, characterized in that the enzyme treatment is carried out within the pH range of about 4-8.

11. A method according to any of the preceding claims, characterized in that the enzyme treatment is carried out at about 10 to 90°C.

12. A method according to claim 11, characterized in that the enzyme treatment is carried out at about 25 - 70 °C.


ISO - BRIGHTNESS (%)
80
75
70
65
IMMEDIATELY
AFTER AGEING
(105°C, 24h)
CONTROL
ENZYME TREATED
(55°C, pH 4,9)
1
2
3
4
H_2O_2 (%)

INTERNATIONAL SEARCH REPORT

PCT/FI 92/00076

International Application N

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 D21C5/00; D21C9/08

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	D21C

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No.[13]
P,A	EP,A,0 430 915 (ENSO-GUTZEIT OY) 5 June 1991 see page 2, line 25 - line 30	1-3,5, 9-12
A	FR,A,2 641 803 (ENSO-GUTZEIT OY) 20 July 1990 cited in the application see page 1, line 28 - page 2, line 7 see page 3, line 1 - line 12 see page 4, line 8 - line 13	1,2,7-12
A	EP,A,0 374 700 (JUJO PAPER CO.) 27 June 1990 cited in the application see page 3, line 8 - line 11	1,2,9-12

° Special categories of cited documents : [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
01 JULY 1992	16.07.92
International Searching Authority EUROPEAN PATENT OFFICE	**Signature of Authorized Officer** BERNARDO NORIEGA F.

Form PCT/ISA/210 (second sheet) (January 1985)

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. FI 9200076 SA 57650

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 01/07/92
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0430915	05-06-91	CA-A-	2030836	28-05-91
		JP-A-	3174079	29-07-91
FR-A-2641803	20-07-90	CA-A-	2007774	16-07-90
		DE-A-	4000558	19-07-90
		JP-A-	2229291	12-09-90
		SE-A-	9000138	17-07-90
EP-A-0374700	27-06-90	JP-A-	2160997	20-06-90
		AU-B-	622738	16-04-92
		AU-A-	4582289	21-06-90
		CA-A-	2005087	13-06-90